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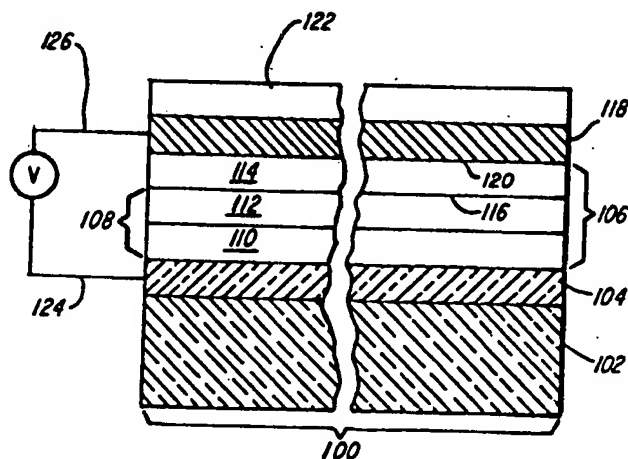
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W-8000 München 90(DE)(54) **Organic electroluminescent device with stabilized cathode.**

(57) An organic electroluminescent device is disclosed which is protected from dark spot formation. The device is comprised of, in sequence, a support, an anode, an organic electroluminescent medium, and a cathode. The cathode contains a plurality of metals, at least one of which is a low work function metal other than an alkali metal. Overlying the cathode is a protective layer comprised of a mixture of at least one organic component of the organic electroluminescent medium and at least one metal having a work function in the range of from 4.0 to 4.5 eV capable of being oxidized in the presence of ambient moisture.

**FIG.1****EP 0 468 440 A2**

This invention relates to organic electroluminescent devices. More specifically, this invention relates to devices which emit light from a current conducting organic layer.

Electroluminescent devices (hereinafter also referred to as EL devices) contain spaced electrodes separated by an electroluminescent medium that emits electromagnetic radiation, typically light, in response to the application of an electrical potential difference across the electrodes. The electroluminescent medium must not only be capable of luminescing, but must also be capable of fabrication in a continuous form (i.e., must be pin hole free) and must be sufficiently stable to facilitate fabrication and to support device operation.

Initially organic EL devices were fabricated using single crystals of organic materials, as illustrated by Mehl et al U.S. Patent 3,530,325 and Williams U.S. Patent 3,621,321. Single organic crystal EL devices were relatively difficult to fabricate and further did not readily lend themselves to thin film constructions.

In recent years preferred organic EL devices have been constructed employing thin film deposition techniques. Using an anode as a device support, the organic electroluminescent medium has been deposited as one or a combination of thin films followed by the deposition of a cathode, also formed as a thin film deposition. Thus, starting with the anode structure, it is possible to form the entire active structure of an organic EL device by thin film deposition techniques. As employed herein the term "thin film" refers to layer thicknesses of less than 5 mm, with layer thicknesses of less than about 2 mm being typical. Examples of organic EL devices containing organic electroluminescent medium and cathode constructions formed by thin film deposition techniques are provided by Tang U.S. Patent 4,356,429, VanSlyke et al U.S. Patents 4,539,507 and 4,720,432, and Tang et al U.S. Patent 4,769,292.

While the art has encountered little difficulty in constructing fully acceptable stable anodes for internal junction organic EL devices, cathode construction has been a matter of extended investigation. In selecting a cathode metal, a balance must be struck between metals having the highest electron injecting efficiencies and those having the highest levels of stability. The highest electron injecting efficiencies are obtained with alkali metals, which are too unstable for convenient use, while metals having the highest stabilities show limited electron injection efficiencies and are, in fact, better suited for anode construction.

Tang U.S. Patent 4,356,429 teaches to form cathodes of organic EL devices of metals such as indium, silver, tin, and aluminum. Van Slyke et al U.S. Patent 4,539,507 teaches to form the cathodes of organic EL devices of metals such as silver, tin, lead, magnesium, manganese and aluminum. Tang et al U.S. Patent 4,885,211 teaches to form the cathodes of organic EL devices of a combination of metals, with at least 50 percent (atomic basis) of the cathode being accounted for by a metal having a work function of less than 4.0 eV.

Despite improvements in the construction of organic EL devices, a persistent problem has been dark spot formation in environments in which the organic EL device is exposed to some level of moisture in the ambient atmosphere. Microscopic analysis of organic EL devices exhibiting dark spot behavior has revealed oxidation of the cathode occurring at its interface with the organic electroluminescent medium. It is believed that the oxidation of the cathode metal at its interface with the organic electroluminescent medium creates a resistive barrier to current flow in affected areas of the organic EL device. Without current flow in an area of the organic EL device, no electroluminescence can occur, and the result is seen as a dark spot when other areas of organic EL device are emitting.

The present invention has as its purpose to minimize, postpone or eliminate the emergence of dark spots in organic EL devices.

In one aspect this invention is directed to an organic electroluminescent device comprised of, in sequence, a support, an anode, an organic electroluminescent medium, and a cathode. The organic electroluminescent device is characterized in that the cathode is comprised of a layer consisting essentially of a plurality of metals other than alkali metals, at least one of the metals having a work function of less than 4 eV and, overlying the cathode, a protective layer comprised of a mixture of at least one organic component of the organic electroluminescent medium and at least one metal having a work function in the range of from 4.0 to 4.5 eV capable of being oxidized in the presence of ambient moisture.

It is a further object of the invention to provide an organic EL device having improved cathode characteristics that is compatible with formation by thin film deposition techniques.

Brief Description of the Drawings

Figure 1 is schematic diagram of an organic EL device according to the invention.

The drawings are necessarily of a schematic nature, since the thicknesses of the individual layers are too thin and thickness differences of the various elements are too greater to permit depiction to scale or to permit convenient proportionate scaling.

An organic electroluminescent (EL) device 100 is shown in Figure 1 consisting of a light transmissive support 102 onto which is coated a light transmissive anode 104. Overlying the anode is an organic electroluminescent medium 106. As shown, the organic electroluminescent medium is divided into (1) a hole injecting and transporting zone 108, which is further divided into (a) a hole injecting layer 110 contacting the anode and (b) an overlying hole transporting layer 112, and (2) an electron injecting and transporting zone 114 forming a junction 116 with the hole transporting layer.

A cathode 118 overlies and forms an electron injecting interface 120 with the organic electroluminescent medium. A protective layer 122 overlies the cathode.

In use the anode 104 and cathode 118 are connected to an external power source V by conductors 124 and 126, respectively. The power source can be a continuous direct current or alternating current voltage source or an intermittent current voltage source. Any convenient conventional power source, including any desired switching circuitry, can be employed which is capable of positively biasing the anode with respect to the cathode. Either the anode or cathode can be at ground potential.

The organic EL device can be viewed as a diode which is forward biased when the anode is at a higher potential than the cathode. Under these conditions injection of holes occurs from the anode into the hole injecting layer 110 of the hole injecting and transporting zone 106. The holes are transported across the hole transporting layer 112 and across the junction 116 into the electron injecting and transporting zone 114. Concurrently electrons are injected from the cathode 118 into the electron injecting and transporting zone 114. When a migrating electron drops from its conduction band potential to a valence band in filling a hole, energy is released as light. Depending upon the choice of alternative constructions, the released light can be emitted from the organic electroluminescent medium through one or more edges of the organic electroluminescent medium separating the electrodes, through the anode and support, through the cathode, or through any combination of the foregoing. Since the organic electroluminescent medium is quite thin, it is usually preferred to emit light through one of the two electrodes. In the preferred form of the EL device shown the anode and support are specifically constructed to be light transmissive, thereby facilitating emission through these elements.

Reverse biasing of the electrodes reverses the direction of mobile charge migration, depletes the organic electroluminescent medium of mobile charge carriers, and terminates light emission. When an AC power source is employed, the internal junction organic EL devices are forward biased during a portion of each period and reverse biased during the remaining portion of the period.

To allow the organic EL device to operate efficiently the cathode must contain at least one metal having a relative low (less than 4.0 eV) work function in contact with the organic electroluminescent medium. Therefore, the lowest work function metal present in the cathode at the interface is particularly susceptible to oxidation. The presence of moisture in the ambient atmosphere surrounding the organic EL device has been observed to lead to oxidation of the cathode low work function metal at its interface with the organic electroluminescent medium, even when a low work function metal is present in only a limited amount or is overcoated with a higher work function metal.

While the susceptibility of the cathode to oxidation is inherent in the materials and operation of the cathode of an efficient organic EL device, there are additional contributing factors. In constructing organic EL devices by thin film forming techniques, the cathode is rarely greater than about 2 mm in thickness, preferably less than about 5000Å in thickness. The thin film deposition techniques, such as vacuum vapor deposition, sputtering and the like, used to form the cathode in these thickness ranges do not produce impervious layers. Microchannels (microscopic local disruptions) are believed to be present in the cathodes that allow moisture migration through the cathode to its interface with the organic electroluminescent medium.

It has been observed that dark spot formation in organic EL devices can be controlled by overcoating the cathode with a protective layer comprised of a mixture of a metal having a work function in the range of from 4.0 to 4.5 eV and at least one organic component of the organic electroluminescent medium. Surprisingly, neither the metal alone nor the the organic component alone have been found to be effective as a protective layer for dark spot reduction. Further, when the metal and organic component are coated successively as superimposed layers, they are also ineffective to stabilize the organic EL device against dark spot formation.

The selection of metals for the protective layer having a work function in the range of from 4.0 to 4.5 eV provides metals that are not so reactive as to create stability concerns during device fabrication, yet are sufficiently reactive to be oxidized by ambient atmospheric moisture over an extended period of time when incorporated into the organic EL device. Representative metals in the preferred work function range include aluminum, vanadium, chromium, iron, cobalt, nickel, copper, zinc, tin, antimony, tantalum and lead. All of these metals can be readily deposited by vacuum vapor deposition, sputtering and similar thin film

deposition techniques. While these metals oxidize slowly as bulk metals, in mixtures, such as those produced by thin film codeposition techniques, the metals exhibit a high surface to volume ratio that enhances their oxidation susceptibility.

The organic material that is mixed with the metal in the protective layer can be any of the various organic materials known to be useful in forming the organic electroluminescent medium of the EL device. The reason for choosing one of the organic materials contained in the organic electroluminescent medium is to provide a practical advantage in device construction. The protective layer can be formed without introducing any requirement for an additional organic material deposition capability. Rather, codeposition of the metal and organic component of the protective layer can be achieved using any of the same materials and deposition procedures employed for producing the organic electroluminescent medium. If, for example, the organic electroluminescent medium is formed by vacuum vapor deposition of a particular organic component, this same deposition procedure can be used again after cathode formation, modified only by the concurrent deposition of the metal component. Since the metal component is preferably supplied independently from a separate source during codeposition, minimal, if any, modification of the organic deposition technique employed during formation of the organic electroluminescent medium is contemplated during codeposition of the protective layer. Usually, only the rate of deposition is varied to achieve the desired proportion of the organic component to the metal component of the protective layer.

The proportion of the metal and organic components of the protective layer can be widely varied. Since the amount of moisture that can be intercepted in route to the cathode is dependent on the amount of metal present in the protective layer, it is generally preferred that the protective layer contain at least about 20 percent of the metal. (Except as otherwise noted, percent is in each instance weight percent, based on total weight.) The minimum amount of the organic component is that required to keep the metal sufficiently dispersed to maintain a high surface to volume ratio. Generally at least 10 percent by weight of the organic component is more than sufficient to accomplish this function. Thus, it is generally preferred that the metal account for from about 20 to 90 percent (optimally from about 30 to 80 percent) of the protective layer with the organic component accounting for from 10 to 80 percent (optimally from about 20 to 70 percent) of the protective layer.

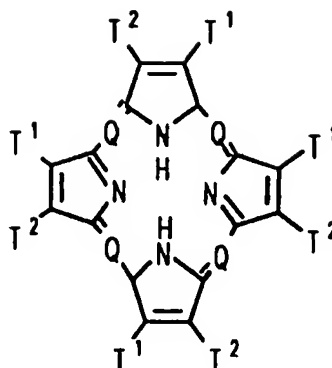
The duration of protection against dark spot formation of the organic EL device is a function of the amount of metal present in the protective layer for any given ambient moisture level. The thickness of the protective layer as well as the proportion of metal in the protective layer determines the total amount of metal present. For short term stabilization any thickness of the protective layer sufficient to provide a continuous coating of the cathode is effective. Generally protective layer thicknesses of at least about 200Å (optimally at least about 500Å) are contemplated to assure continuous coverage of the cathode. Maximum protective layer thicknesses are a function of coating convenience. Using thin film deposition techniques thicknesses up to about 2 μm (optimally up to about 1 μm) are preferred for the protective layer.

The cathode of the organic EL device can be constructed of any conventional metal or combination of metals, other than an alkali metal (excluded as being too unstable), provided at least one of the metals present exhibits a low work function--that is, less than about 4.0 eV. If no low work function metal is present, the organic EL device will have a reduced capability of injecting electrons into the organic electroluminescent medium and consequently a relatively low efficiency. Preferred cathodes are those constructed of a combination of a metal having a low (<4.0 eV) work function and one other metal, preferably a metal having a work function greater than 4.0 eV. The metals can be employed in extremely wide proportions, ranging from about 1 percent to 99 percent of the low work function metal with another metal, preferably a higher work function metal (e.g., a metal having a work function >4.0 eV), forming the balance of the cathode. The combinations of metals taught by Tang et al U.S. Patent 4,885,211, here incorporated by reference, are specifically contemplated for construction of the cathodes of this invention. The Mg:Ag cathodes of Tang et al U.S. Patent 4,885,211 constitute one preferred cathode construction. Aluminum and magnesium cathodes with magnesium constituting at least 0.05 (preferably at least 0.1) percent and aluminum constituting at least 80 (preferably at least 90) percent constitute another preferred cathode construction. The aluminum and magnesium cathodes are the subject matter of the VanSlyke et al (I) concurrently filed patent application cited above.

The anode of the organic EL device can take any convenient conventional form. Typically the anode is constructed of one or a combination of metals having a work function in excess of 4.0 eV. Metals having work functions >4.0 eV are listed by Tang et al U.S. Patent 4,885,211, incorporated by reference above. When, as is preferred, luminescence is intended to occur through the anode, it is preferred to construct the anode of one or a combination of light transmissive metal oxides, such as indium oxide, tin oxide or, optimally, indium tin oxide (ITO).

As employed herein the term "light transmissive" means simply that the layer or element under

(II)



Highly preferred examples of useful porphyrinic compounds are metal free phthalocyanines and metal containing phthalocyanines. While the porphyrinic compounds in general and the phthalocyanines in particular can contain any metal, the metal preferably has a positive valence of two or higher. Exemplary preferred metals are cobalt, magnesium, zinc, palladium, nickel, and, particularly, copper, lead, and platinum.

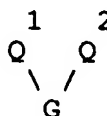
Illustrative of useful porphyrinic compounds are the following:

- PC-1 Porphine
- PC-2 1,10,15,20-Tetraphenyl-21H,23H-porphine copper (II)
- PC-3 1,10,15,20-Tetraphenyl-21H,23H--porphine zinc (II)
- PC-4 5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphine
- PC-5 Silicon phthalocyanine oxide
- PC-6 Aluminum phthalocyanine chloride
- PC-7 Phthalocyanine (metal free)
- PC-8 Dilithium phthalocyanine
- PC-9 Copper tetramethylphthalocyanine
- PC-10 Copper phthalocyanine
- PC-11 Chromium phthalocyanine fluoride
- PC-12 Zinc phthalocyanine
- PC-13 Lead phthalocyanine
- PC-14 Titanium phthalocyanine oxide
- PC-15 Magnesium phthalocyanine
- PC-16 Copper octamethylphthalocyanine

The hole transporting layer of the organic EL device contains at least one hole transporting aromatic tertiary amine, where the latter is understood to be a compound containing at least one trivalent nitrogen atom that is bonded only to carbon atoms, at least one of which is a member of an aromatic ring. In one form the aromatic tertiary amine can be an arylamine, such as a monoarylamine, diarylamine, triarylamine, or a polymeric arylamine. Exemplary monomeric triarylaminines are illustrated by Klupfel et al U.S. Patent 3,180,730. Other suitable triarylaminines substituted with vinyl or vinylene radicals and/or containing at least one active hydrogen containing group are disclosed by Brantley et al U.S. Patents 3,567,450 and 3,658,520.

A preferred class of aromatic tertiary amines are those which include at least two aromatic tertiary amine moieties. Such compounds include those represented by structural formula (III):

(III)



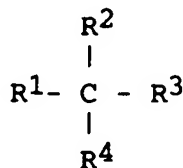
wherein

Q¹ and Q² are independently aromatic tertiary amine moieties and

G is a linking group such an arylene, cycloalkylene, or alkylene group or a carbon to carbon bond.

A particularly preferred class of triaryl amines satisfying structural formula (III) and containing two triarylamine moieties are those satisfying structural formula (IV):

(IV)

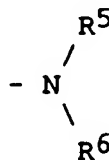


where

R¹ and R² each independently represents a hydrogen atom, an aryl group or alkyl group or R¹ and R² together represent the atoms completing a cycloalkyl group and

R³ and R⁴ each independently represents an aryl group which is in turn substituted with a diaryl substituted amino group, as indicated by structural formula (V):

(V)

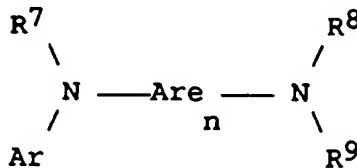


wherein R⁵ and R⁶ are independently selected aryl groups.

Another preferred class of aromatic tertiary amines are tetraaryldiamines. Preferred tetraaryldi- amines include two diarylamino groups, such as indicated by formula (V), linked through an arylene group.

Preferred tetraaryldiamines include those represented by formula (VI).

(VI)



wherein

Are is an arylene group,

n is an integer of from 1 to 4, and

Ar, R⁷, R⁸, and R⁹ are independently selected aryl groups.

The various alkyl, alkylene, aryl, and arylene moieties of the foregoing structural formulae (III), (IV), (V), and (VI) can each in turn be substituted. Typical substituents including alkyl groups, alkoxy groups, aryl groups, aryloxy groups, and halogen such as fluoride, chloride, and bromide. The various alkyl and alkylene moieties typically contain from about 1 to 5 carbon atoms. The cycloalkyl moieties can contain from 3 to about 10 carbon atoms, but typically contain five, six, or seven ring carbon atoms--e.g., cyclopentyl, cyclohexyl, and cycloheptyl ring structures. The aryl and arylene moieties are preferably phenyl and phenylene moieties.

Representative useful aromatic tertiary amines are disclosed by Berwick et al U.S. Patent 4,175,960 and